[DESCRIPTION]

FIELD OF THE INVENTION

The present invention relates to a negative-working heat-sensitive material which is suitable for making a lithographic printing plate by direct-to-plate recording and to a method for imaging said heat mode recording material by means of an infrared laser.

BACKGROUND OF THE INVENTION

Lithographic printing is the process of printing from specially prepared surfaces, which contain a lithographic image consisting of areas that are capable of accepting ink (oleophilic areas) and areas that do not accept ink but are water-accepting (hydrophilic areas). In so-called wet lithographic printing methods, both water or an aqueous dampening liquid (also called fountain solution) and ink are applied to the plate surface that contains the hydrophilic and oleophilic areas. The hydrophilic areas are soaked with water or the dampening liquid and are thereby rendered oleophobic.

Various heat-mode plate materials are known which can be used as a lithographic master for printing with greasy inks. Ablative plates are the best known examples of so-called processless plates, i.e. plates which do not require any processing and therefore can be used as a printing plate immediately after exposure. The heat, which is generated in the recording layer of such ablative plates by light absorption of a laser beam, removes a hydrophilic or oleophilic topcoat to expose an underlying oleophilic respectively hydrophilic surface, thereby obtaining the necessary differentiation of ink-acceptance between the image (printing) and non-image or background (non-printing) areas.

For example DE-A-2 448 325 [illegible]

obtained which can be used on an printing press without further processing. The plate is called a "direct negative" plate because it is suitable for direct exposure by a laser beam (no film applied to plate, no film mask required) and because the areas of the recording material that have been exposed to the laser are rendered ink-accepting and define the image areas, i.e. the printing areas.

Other disclosures in **DE-A-2 448 325** concern "direct negative" printing plates comprising e.g. hydrophilic aluminum support coated with a water soluble laser light (Argon-488nm) absorbing dye or with a coating based on a mixture of hydrophilic polymer and laser light absorbing dye (Argon-488nm). Further examples of such heat-mode recording materials for preparing "direct negative" printing plates have been described in e.g. **DE-A-2 607 207, DD-A-213 530, DD-A-217 645** and **DD-A-217 914**. These documents disclose heat-mode recording materials that contain an anodized aluminum support and a hydrophilic recording layer provided thereon. Laser exposure renders the exposed areas insoluble and ink-receptive, whereas the non-exposed areas remain hydrophilic and water-soluble. Such plates can also be used directly on the press without processing, because the non-exposed areas are removed by the dampening liquid during printing, thereby revealing the anodized aluminum support.

DD-A-155 407 discloses a processless heat-mode "direct negative" printing plate where a hydrophilic aluminum oxide layer is rendered oleophilic by direct laser heat-mode imaging.

The above heat-mode "direct negative" lithographic printing plate are characterized by a low recording speed and/or the obtained plates are of poor quality and durability.

EP-A-580 393 discloses an ablative lithographic printing plate directly imageable by laser discharge, the plate comprising a topmost first layer and a second layer underlying the first layer wherein the first layer is characterized by efficient absorption of infrared radiation and the first and second layer exhibit different affinities for at least one printing liquid.

EP-A-683 728 discloses a heat mode recording material comprising on a support having an ink accepting surface or being coated with an ink accepting layer a substance capable of converting light into heat and a hardened hydrophilic surface layer having a thickness not more than 3 µm.

US 4,034,183 describes a processless lithographic printing plate that comprises a light-absorbing hydrophilic top layer coated on a support which is exposed to a laser beam to convert the exposed areas from an ink repelling to an ink receptive state. All of the examples and teachings require a high power laser and the run lengths of the resulting lithographic plates are limited.

US 3,832,948 describes both a printing plate with a hydrophilic layer that may be ablated by strong light from a hydrophobic support and also a printing plate with a hydrophobic layer that may be ablated from a hydrophilic support. However, no examples are given.

US 3,964,389 describes a processless printing plate based on the principle of laser transfer of material. This process is very sensitive to transfer defects and requires an additional donor sheet.

US 4,054,094 describes a process for making a lithographic printing plate by using a laser beam to etch away a thin top coating of polysilicic acid on a polyester base, thereby rendering the exposed areas receptive to ink. No details of run length or print quality are given, but it is expected that an non-crosslinked polymer such as polysilicic acid will wear off rapidly and give a short run length.

US 4,081,572 describes a method for preparing a printing master on a substrate by coating the substrate with a hydrophilic polyamic acid and then image-wise converting the polyamic acid to melanophilic polyimide with heat from a flash lamp or a laser. No details of run length, image quality or ink water balance are given.

Japanese Kokai No. 55/105560 describes a method of preparation of a lithographic printing plate by laser beam removal of a hydrophilic layer coated on a melanophilic support, in which the hydrophilic layer contains colloidal silica, colloidal alumina, a carboxylic acid, or a salt of a carboxylic acid. The only examples given use colloidal alumina alone [illegible] with no crosslinkers or additives. No details are given for the ink water balance or limitations on run length.

WO 92/09934 [illegible]
[illegible] polymer with

acid labile tetrahydropyranyl groups. This would include a hydrophobic-hydrophilic switching lithographic plate [illegible]. However, such a polymeric switch is [illegible] differentiation between hydrophilic and oleophilic areas.

All the examples mentioned in the prior art fail to prepare a processless direct image-able printing plate which has a high sensitivity, good start-up behaviour and offers a high run length.

Unpublished EP-A no. 99202109, filed on 29.06.99, discloses a negative-working heat-sensitive material for making lithographic plates comprising in the order given a lithographic base having a hydrophilic surface, an oleophilic imaging layer and a cross-linked hydrophilic upper layer. The heat generated during exposure in the imaging layer removes the hydrophilic upper layer by ablation. However, the water-acceptance of the non-exposed areas is insufficient and, as a result, the plate has an inferior start-up behaviour, i.e. the non-exposed areas to a certain extent accept ink (a defect known as "toning") while printing the first 10 to 50 copies, which are lost due to bad print quality.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a processless material that is suitable for heat-mode direct-to-plate recording and is characterized by a high lithographic quality, especially with regard to start-up behaviour. This object is realized by the material defined in claim 1. Preferred embodiments thereof are defined in the dependent claims.

DETAILED DESCRIPTION OF THE INVENTION

The lithographic printing plate of the present invention comprises in the order given a lithographic base having a hydrophilic surface, an oleophilic imaging layer and a cross-linked hydrophilic upper layer.

The cross-linked hydrophilic upper layer is preferably [illegible]

carboxymethyl cellulose along with suitable crosslinking or modifying agents including e.g. hydrophilic organic titanium reagents, aluminium formyl acetate, dimethylol urea, melamine, aldehydes, hydrolyzed tetraalkyl orthosilicate etc. Suitable hydrophilic binders for use in the upper layer may be selected from the group consisting of gum arabic, casein, gelatin, starch derivatives, carboxymethyl cellulose and the salts thereof, cellulose acetate, sodium alginate, vinyl acetate-maleic acid copolymers, styrene-maleic acid copolymers, polyacrylic acids and salts thereof, polymethacrylic acids and salts thereof, hydroxyethylene polymers, polyethylene glycols, hydroxypropylene polymers, polyvinyl alcohols and hydrolyzed polyvinylacetate having a hydrolysis degree of at least 60% by weight and more preferably at least 80% by weight.

Hydrophilic layers containing polyvinylalcohol or polyvinylacetate hydrolyzed to an extent of at least 60% by weight hardened with a tetraalkyl orthosilicate e.g. tetraethyl orthosilicate or tetramethyl orthosilicate as disclosed in e.g. **US 3,476,937,** are particularly preferred because their use in the present heat-mode recording material results in excellent lithographic printing properties.

A further suitable cross-linked hydrophilic layer is disclosed in **EP-A- 514 990.** The layer disclosed in this EP-application comprises the hardening reaction product of a (co)polymer containing amine or amide functions having at least one free hydrogen e.g. amino modified dextrans and aldehyde.

The cross-linked hydrophilic upper layer preferably also contains substances that increase the mechanical strength and the porosity of the layer e.g. metal oxide particles which are particles of titanium dioxide or other metal oxides. Incorporation of these particles gives the surface of the cross-linked hydrophilic layer a uniform rough texture consisting of microscopic hills and valleys. These particles are preferably oxides or hydroxides of beryllium, magnesium, aluminium, silicon, gadolinium, germanium, arsenic, indium, tin, antimony, tellurium, lead, bismuth or a transition metal. Particularly preferred particles are oxides or hydroxides of aluminium, silicon, zirconium and titanium used in [illegible] by weight of the hydrophilic layer, more preferably in [illegible] by weight of the hydrophilic layer.

According to the present invention the addition [illegible] to the cross-linked hydrophilic upper layer of an organic compound comprising a sulfonic acid ($-SO_3H$), sulfuric acid ($-OSO_3H$), phosphonic acid ($-PO_3H_2$) or phosphoric acid ($-OPO_3H_2$) [illegible] an improved starting behaviour which is comparable to a conventional plate wherein an electrochemically grained and anodized lithographic aluminum substrate defines the non printing areas. This effect is obtained even when only a small amount of said organic compound is added to the cross-linked hydrophilic upper layer, e.g. an amount between 0.5% and 20% by weight of the dry hydrophilic layer and more preferably between 1% and 15% by weight.

More particularly, said organic compound comprises an organic radical corresponding to one of the following formula :

$$R1-(O)_n-PO_3A_2 \quad (I)$$

$$R2-(O)_n-SO_3A \quad (II)$$

wherein n is 0 or 1 and A is hydrogen, a counter ion or an alkyl group. In formula I, both A groups can have any of the latter meanings independently from one another or can together represent a divalent counter ion or an alkylene group. R1 and R2 are an organic radical. R1 can be a low molecular or a macromolecular radical. R2 is a macromolecular organic radical. The term "macromolecular radical" comprises polymers, copolymers, dendrimers, hyperbranched polymers, oligomers and multifunctional compounds preferably having a molecular weight higher than 500 g/mol. Preferred examples of such macromolecular compounds are : polystyrene sulfonic acid, polyvinylphosphonic acid, polyvinyl methylphosphonic acid, phosphoric acid esters of polyvinyl alcohol, polyvinylsulfonic acid, polyvinylbenzenesulfonic acid, sulfuric acid esters of polyvinyl alcohol, acetals of polyvinyl alcohol formed by reaction with a sulfonated aliphatic aldehyde [illegible] ; [illegible] aldehyde.

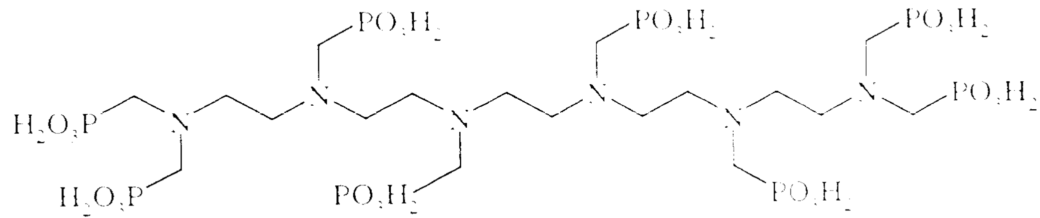
[illegible]

phosphonic acid, phosphonated maleic anhydride, [illegible] acrylates or methacrylates, dimethyl vinylphosphonate, [illegible] phosphonic acid, phosphonomethylated vinylamine [illegible] methylated vinylamines, vinyl amino methylene phosphonic acid, 1-phenyl vinyl phosphonic acid, vinyl phosphonic acid, acrylamido methylpropyl phosphonic acid, methyl vinylphosphonate, mono-vinyl ester of phosphoric acid (vinyl phosphate), mono-allyl ester of phosphoric acid (allyl phosphate), 2-propenyl-phosphonic acid (allylphosphonic acid), 2-methyl-[illegible]ethyl ester of 2-propenoic acid, [illegible] ester of 2-propenoic acid, 2-Acrylamido-2-methyl-1-propanesulfonic acid (AMPS), sulfoisophthalic acid, sulfoethyl methacrylate, 2-(sodiosulfo) ethylmethacrylate, ω-sulfoxyalkyl acrylates or methacrylates, styrene sulfonic acid, diazosulphonate monomers like methacrylamidophenyl diazosulphonate, allyl ethoxy sulphates, 1-allyloxy-2-hydroxypropyl sulphonate, vinylsulfonic acid, Sulfuric acid mono-ethenyl ester (vinyl sulfuric acid), mono-2-propenyl ester of sulfuric acid, Sulfuric acid monovinyl ester (vinyl sulfuric acid), Sulfatoethyl methacrylate (Bisomer SEM), Methacrylic acid 2-hydroxyethanesulfonic acid ester (Sulfoethyl methacrylate = SEM) and their salts. Typical useful sulfonated polymers can be obtained from e.g. Alco Chemical (division of National Starch and Chemical Company) e.g. with the trade names [illegible], Aquatreat AR-540, Aquatreat AR-546, Aquatreat AR-545. Other applicable sulfonic acid polymers are e.g. methylene coupled condensation products of arylsulphonic acid e.g. available from Bayer under the trade name Baykan [illegible] or sulphoisophthalic acid based polyesters e.g. available from Eastman Chemical Company or Agfa. Other useable sulfate containing polymers are [illegible] e.g. [illegible] copolymer with AMPS [illegible] obtained from [illegible] copolymer with [illegible] sulphonic acid [illegible] salt). Other useful polymers are polymer derivatives [illegible]

[illegible]

imines, etc. Besides traditional homopolymers and copolymers also branched macromolecules like hyperbranched polymers or dendrimers could be applied.

In particular multifunctional phosphonates with the trade name Briquest are highly preferred. One of the suitable examples is Briquest 8106-25S = [[3,6,9,12-tetrakis(phosphonomethyl)-3,6,9,12-tetraaza tetradecane-1,14-diyl]bis[nitrilobis(methylene)]]tetrakis-Phosphonic acid sodium salt:

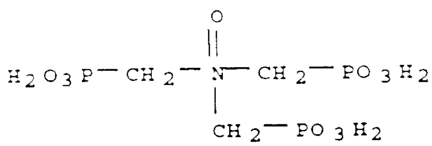


· x Na

wherein x is an integer between zero and the total number of acid protons in the molecule. Other suitable Briquest grades are: Briquest 3010-25K ([(oxidonitrilo)tris(methylene)]tris-Phosphonic acid, potassium salt), Briquest 281-25S ([[(2-ethylhexyl)imino]bis(methylene)]bis-Phosphonic acid, sodium salt), Briquest 421-[illegible]N ([1,2-ethanediylbis[nitrilobis(methylene)]]-tetrakis-Phosphonic acidtetraammonium salt), Briquest 785 ([[(phosphonomethyl)imino]bis[2,1-ethanediyl[(phosphonomethyl)imino]-2,1-ethanediylnitrilobis(methylene)]]-Phosphonic acid, tetrakis-, sodium salt), Briquest ADPA-[illegible]AW ((1-hydroxyethylidene)bis-Phosphonic acid, potassium salt), Briquest 543 ([bis[2-[bis(phosphonomethyl)amino]ethyl]amino]methyl)-Phosphonic acid sodium salt), Briquest 5[illegible] ([[(2-hydroxyethyl)imino]bis(methylene)]bis-Phosphonic acid, sodium salt), Briquest [illegible] ([nitrilotris(methylene)]tris-Phosphonic acid, sodium salt), Briquest [illegible] ([nitrilotris(methylene)]tris-Phosphonic acid), Briquest ADPA-[illegible]A ((1-hydroxyethylidene)bis-Phosphonic acid), [illegible]

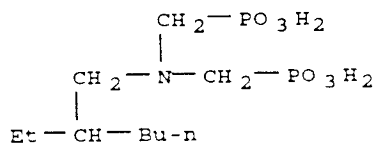
[illegible]

Briquest [illegible] :



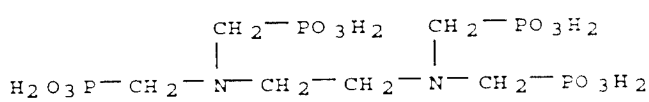
· x K

Briquest [illegible] :



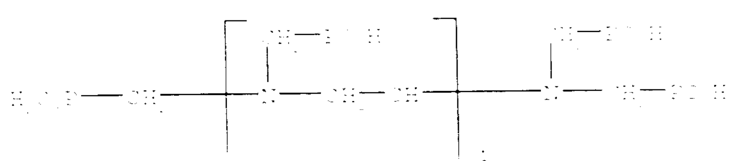
· x Na

Briquest [illegible] :



· 4 NH_3

Briquest [illegible] :



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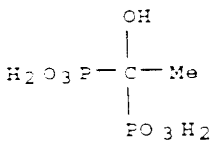

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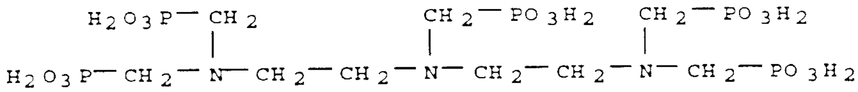
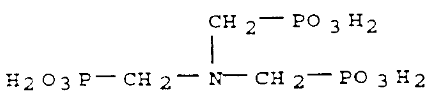
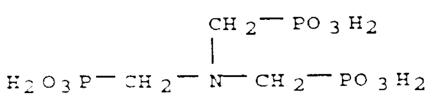


· x Na

Briquest [illegible] :

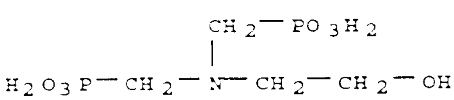


Briquest [illegible] :



· x Na

Briquest [illegible] :



· x Na

[illegible]

The [illegible] cross-linked hydrophilic [illegible] layer [illegible] additional [illegible] [illegible]. The [illegible] cross-linked hydrophilic [illegible] [illegible]. Particular examples of suitable [illegible] cross-linked hydrophilic [illegible] layers for use in accordance with the present invention are [illegible] in EP-A- 601 240, GB-P- 1 419 512, FR-P- 2 300 354, US-P- 3 971 660, and US-P- 4 284 705.

The [illegible] layer [illegible] capable of converting light into heat.

Suitable compounds capable of converting light into heat are preferably infrared absorbing [illegible] in the wavelength range of the light source used for image-wise exposure. Particularly useful compounds are for example dyes and in particular infrared dyes as disclosed in EP-A- 908 307 and pigments and in particular infrared pigments such as carbon black, metal carbides, borides, nitrides, carbonitrides, bronze-structured oxides. It is also possible to use conductive polymer dispersion such as polypyrrole, polyaniline or polythiophene-based conductive polymer dispersions. Carbon black or graphite yield very good and favorable results.

The binder of the [illegible] layer is preferably selected from the group consisting of [illegible] polyesters, polyurethanes, novolac, polyvinyl [illegible] or copolymers or mixtures thereof. [illegible] the binder itself is [illegible] [illegible] disclosed in GB-P-1 316 398 and DE-A- 2 512 038; [illegible] polymer [illegible]. Also [illegible] of liberating [illegible] are [illegible].

The [illegible] layer [illegible] [illegible]

or stearic acid in isopropyl alcohol [illegible] chromium complexes. Dupont [illegible] April [illegible].

The dry coating weight of the oleophilic imaging layer is preferably between [illegible] and [illegible] g/m², more preferably between [illegible] and [illegible] g/m². If the oleophilic imaging layer is too thin (< [illegible] g/m²), the oleophilicity of the exposed areas is low due to the underlying lithographic base and the run length is mainly limited by the exposed areas. If the IR-sensitive oleophilic layer is too thick (> [illegible] g/m²) the effect of the hydrophilic surface of the lithographic base is lost and the run length may be limited by the non-exposed areas due to toning.

According to the present invention the lithographic base may be an anodized aluminum support. A particularly preferred lithographic base is an electrochemically grained and anodized aluminum support. The anodized aluminum support may be treated to improve the hydrophilic properties of its surface. For example, the aluminum support may be silicated by treating its surface with a sodium silicate solution at elevated temperature, e.g. 95°C. Alternatively, a phosphate treatment may be applied which involves treating the aluminum oxide surface with a phosphate solution that may further contain an inorganic fluoride. Further, the aluminum oxide surface may be rinsed with a citric acid or citrate solution. This treatment may be carried out at room temperature or may be carried out at a slightly elevated temperature of about 30 to 50°C. A further interesting treatment involves rinsing the aluminum oxide surface with a bicarbonate solution. Still further, the aluminum oxide surface may be treated with polyvinylphosphonic acid, polyvinylmethylphosphonic acid, phosphoric acid esters of polyvinyl alcohol, polyvinylsulfonic acid, polyvinylbenzenesulfonic acid, sulfuric acid esters of polyvinyl alcohol, and acetals of polyvinyl alcohols formed by reaction with a sulfonated aliphatic aldehyde. It is further evident that one or more of these post treatments may be carried out alone or in combination. More detailed descriptions of these treatments are given in GB-A- 1 084 070, DE-A- 4 423 140, DE-A- 4 417 907, EP-A- 659 909, EP-A- 537 633, DE-A- 4 001 466, EP-A- 292 801, EP-A- 291 760 and US-P- 4 458 005.

[illegible]

which is provided with a hydrophilic layer, hereinafter called 'base layer'. The flexible support is e.g. paper, plastic film or aluminum. The base layer is preferably a cross-linked hydrophilic layer obtained from a hydrophilic binder cross-linked with a hardening agent such as formaldehyde, glyoxal, polyisocyanate or a hydrolyzed tetra-alkylorthosilicate. The latter is particularly preferred.

The hydrophilic binder for use in the base layer is e.g. a hydrophilic (co)polymer such as homopolymers and copolymers of vinyl alcohol, acrylamide, methylol acrylamide, methylol methacrylamide, acrylate acid, methacrylate acid, hydroxyethyl acrylate, hydroxyethyl methacrylate or maleic anhydride vinylmethylether copolymers. The hydrophilicity of the (co)polymer or (co)polymer mixture used is preferably the same as or higher than the hydrophilicity of polyvinyl acetate hydrolyzed to at least an extent of 60% by weight, preferably 80% by weight.

The amount of hardening agent, in particular tetraalkyl orthosilicate, is preferably at least 0.2 parts per part by weight of hydrophilic binder, more preferably between 0.5 and 5 parts by weight, most preferably between 1 parts and 3 parts by weight.

The hydrophilic base layer may also contain substances that increase the mechanical strength and the porosity of the layer. For this purpose colloidal silica may be used. The colloidal silica employed may be in the form of any commercially available water dispersion of colloidal silica for example having an average particle size up to 40 nm, e.g. 20 nm. In addition inert particles of larger size than the colloidal silica may be added e.g. silica prepared according to Stöber as described in J. Colloid and Interface Sci., Vol. 26, 1968, pages 62 to 69 or alumina particles or particles having an average diameter of at least 100 nm which are particles of titanium dioxide or other heavy metal oxides. By incorporating these particles the surface of the hydrophilic base layer is given a uniform rough texture consisting of microscopic hills and valleys, which serve as storage places for water in background areas.

The thickness of the hydrophilic base layer may vary in the range of 0.2 to 25 µm and is preferably 1 to 10 µm.

Particular examples of suitable hydrophilic [illegible] layers for use in accordance with the present invention are disclosed in EP-A- 601 240 GB-P- 1 419 512 FR-P- 2 300 354 US-P- 3 971 660 and US-P- 4 284 705.

As flexible support of a lithographic base in connection with the present embodiment it is particularly preferred to use a plastic film e.g. polyethylene terephthalate film, polyethylene naphthalate film, cellulose acetate film, polystyrene film, polycarbonate film, etc. The plastic film support may be opaque or transparent.

It is particularly preferred to use a film support to which an adhesion improving layer, also called substrate layer, has been provided. Particularly suitable adhesion improving layers for use in accordance with the present invention comprise a hydrophilic binder and colloidal silica as disclosed in EP-A- 619 524, EP-A- 620 502 and EP-A- 619 525. Preferably, the amount of silica in the adhesion improving layer is between 200 mg per m^2 and 750 mg per m^2. Further, the ratio of silica to hydrophilic binder is preferably more than 1 and the surface area of the colloidal silica is preferably at least 300 m^2 per gram, more preferably at least 500 m^2 per gram.

Optionally the heat-sensitive imaging material can be covered with an additional hydrophilic layer, provided on top of the hydrophilic upper layer discussed above, which comprises an organic compound containing cationic groups as described in EP-A no. 99202110, filed on 29.06.99.

In accordance with the method of the present invention, the imaging material is image-wise exposed to cause removal of the cross-linked hydrophilic upper layer and whereby the exposed areas are converted to oleophilic areas while the unexposed areas remain hydrophilic. This is mostly the case when using short pixel dwell times, for example [illegible]. However when using longer pixel dwell times, for example [illegible], the hydrophilic layer may not completely be removed upon exposure. [illegible]

treatment such as rubbing or brushing the layer with [illegible] bath. A preferred additional wet processing step is a gumming step as is normally used for conventional plates. A gumming step is normally not regarded as a processing step but rather as a treatment which protects the hydrophilic areas from fingerprints or other contamination which may affect the water-acceptance of these areas. Upon gumming the remaining ablation dust on the plate is removed thereby avoiding contamination of the press. At the same time the hydrophilic areas are covered with a thin layer of the gumming solution inducing a better start-up performance.

Image-wise exposure in connection with the present invention is preferably an image-wise scanning exposure involving the use of a laser or L.E.D. Preferably lasers are used that operate in the infrared or near-infrared, i.e. wavelength range of 700-1500 nm. Most preferred are laser diodes emitting in the near-infrared with an intensity higher than 0.1 mW/μm^2.

According to the present invention the plate is then ready for printing without an additional development and can be mounted on the printing press.

According to a further method the imaging material is first mounted on the printing cylinder of the printing press and then image-wise exposed directly on the press by means of an integrated image recording device. Subsequent to exposure, the imaging material is ready for printing.

The printing plate of the present invention can also be used in the printing process as a seamless sleeve printing plate. In this option the printing plate may be soldered in a cylindrical form by means of a laser. This cylindrical printing plate which has as diameter the diameter of the print cylinder can be slid on the print cylinder instead of mounting a conventional printing plate. More details on sleeves are given in "Grafisch Nieuws" ed. 15, 1995, page 4 to 6.

The following examples illustrate the present invention without limiting it thereto. All parts and percentages are by weight unless otherwise specified.

EXAMPLES

Reference comparative example

Preparation of the lithographic base

A 0.30 mm thick aluminum foil was degreased by immersing the foil in an aqueous solution containing 5 g/l of sodium hydroxide at 50°C and rinsed with demineralized water. The foil was then electrochemically grained using an alternating current in an aqueous solution containing 4 g/l of hydrochloric acid, 4 g/l of hydroboric acid and 5 g/l of aluminum ions at a temperature of 35°C and a current density of 1200 A/m^2 to form a surface topography with an average center-line roughness Ra of 0.5 µm.

After rinsing with demineralized water the aluminum foil was etched with an aqueous solution containing 300 g/l of sulfuric acid at 60°C for 180 seconds and rinsed with demineralized water at 25°C for 30 seconds.

The foil was subsequently subjected to anodic oxidation in an aqueous solution containing 200 g/l of sulfuric acid at a temperature of 45°C, a voltage of about 10 V and a current density of 150 A/m^2 for about 300 seconds to form an anodic oxidation film of 3.00 g/m^2 of Al_2O_3, then washed with demineralized water, post-treated with a solution containing polyvinylphosphonic acid and a solution containing aluminum trichloride, and subsequently rinsed with demineralized water at 20°C during 120 seconds and dried.

Preparation of the oleophilic imaging layer

The imaging layer was coated on the lithographic base at a wet coating thickness of 20 µm from a solution having the following composition:

[illegible] carbon black dispersion of the following composition:

[illegible]

[illegible]

[illegible]

[illegible]

[illegible] of the following composition:

- 1.4[illegible] g Nitrocellulose E[illegible] (trade mark from Wolff Walsrode)
- 11.7[illegible] g Ethylacetate

[illegible] g Transition metal complex of the following composition :

- [illegible].18 g [illegible] (trade mark from [illegible])
- 2.44 g isopropanol

2.12 g Cymel solution of the following composition :

- [illegible].42 g Cymel 301 (trade mark from Dyno Cytec)
- 1.7[illegible] g Ethylacetate

[illegible] g p-toluene sulfonic acid solution of the following composition :

- [illegible] g p-toluene sulfonic acid
- [illegible].484 g Ethylacetate

29[illegible].6[illegible] g Ethylacetate

2[illegible].[illegible] g Butylacetate

Preparation of the cross-linked hydrophilic upper layer

After drying the imaging layer, the hydrophilic layer was coated to a wet coating thickness of [illegible] µm from a solution having the following composition :

[illegible] g [illegible]% SiO2 dispersion (Kieselsol [illegible] from Bayer) in water, stabilized with Polyviol WX 48[illegible] (polyvinyl alcohol from Wacker); the dispersion contained [illegible] % polyvinyl alcohol versus SiO2 (average particle size [illegible] nm)

[illegible] g [illegible]% hydrolysed tetramethyl orthosilicate (TMOS) in water ethanol [illegible].

1.[illegible] g [illegible]% wetting agent in water.

The pH of this solution was adjusted to 4 prior to coating. After coating, the layer was hardened for 12 hours at [illegible]°C / 50% R.H.

Example [illegible] (comparison)

[illegible]

added to the coating solution of the hydrophilic layer. The details are given in table 1.

The resulting imaging materials were [illegible] Trendsetter 3244T ™ at 24[illegible] dpi operating at a [illegible] speed [illegible] rpm and a laser output of 1[illegible] Watt. After imaging the plate was mounted on a Heidelberg GTO52 press with a Dahlgren dampening system using K+E 800 Skinnex as ink and Rotamatic as dampening liquid. A compressible blanket was used. Subsequently the press was started by allowing the print cylinder with the imaging material mounted thereon to rotate. The dampener rollers of the press were first dropped on the imaging material so as to supply dampening liquid to the imaging material and after 10 revolutions of the print cylinder, the ink rollers were dropped to supply ink. After 10 further revolutions, the paper supply was started.

The start-up behaviour is defined as the number of sheets required before toning-free prints were obtained. The results are summarized in table 1.

Examples 4-7

The materials 4, 5, 6 and 7 were prepared in an identical way as the reference material with the proviso that in the solution of the hydrophilic layer a part of the polyvinylalcohol was replaced by a polymer which contains a sulfonic acid pendant group resulting in a layer composition as shown in table 1. The exposure, printing and evaluation method was the same as used in the [illegible] examples 1-3.

Examples 8 and 9

The materials 8 and 9 were prepared in an identical way as the reference material with the proviso that polymers which contain a sulfonic acid pendant group [illegible] of the hydrophilic layer resulting in a layer composition as shown in table 1. The exposure, printing and evaluation method was the same as used in the [illegible]

Table 1 : Start up behaviour of Examples 1, 2 and 3

Example	Composition hydrophilic layer				Start up
	[illegible]	TMOS	polyvinylalcohol	extra binder	
[illegible]	[illegible] %	35.5 %	7.0 %		100 prints
[illegible]	[illegible] %	[illegible] %	7.0 %	3.5 % PSSA [1]	5 prints
[illegible]	[illegible] %	[illegible] %	7.0 %	3.5 % PVPA [2]	10 prints
[illegible]	[illegible] %	29.5 %	7.0 %	[illegible].5 % Briquest 8106-25S [3]	10 prints

[1] polystyrenesulfonic acid; Mn = 100000 g/mol; Mw = 200000 g/mol
[2] polyvinylphosphonic acid; Mn = 6600 g/mol; Mw = 30000 g/mol
[3] commercially available from Albright & Wilson

Table 2 : Start up behaviour of Examples 4, 5, 6 and 7

Example	Composition hydrophilic layer				Start up
	[illegible]	TMOS	polyvinylalcohol	PSSA (footnote 1 of Table 1)	
[illegible]	[illegible] %	[illegible] %	7.0 %	[illegible] %	[illegible] prints
[illegible]	[illegible]	[illegible]	[illegible] %	[illegible] %	[illegible] prints
[illegible]	[illegible]	[illegible]	[illegible].5 %	[illegible].5 %	[illegible] prints
[illegible]	[illegible] %	[illegible] %	2.0 %	[illegible].0 %	[illegible] prints
7	[illegible] %	[illegible] %	[illegible].0 %	7.0 %	5 prints

Table [illegible]: Starting behaviour of Examples 4 and [illegible]

Example	Composition hydrophilic layer				Starting
	[illegible]	TMOS	polyvinylalcohol	extra binder	
[illegible]	[illegible]	[illegible] %	7.0 %	[illegible]	[illegible] prints
[illegible]	[illegible]	[illegible]	6.5 %	[illegible] % Versa TL [illegible] [1]	5 prints
[illegible]	[illegible] %	24.0 %	6.5 %	6.5 % PSSA	[illegible] prints

[illegible] (PSSA) commercially available from National Starch & Chem. Corp.

[illegible] Versa TL [illegible].